OIPE JUL 28 2003 PATENT & TRADEMARK OFFICE

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JUL 31 2003
TC 1700

#12

09/580270

FILE NO. 33219-PCT-USA-A
(070338.0582)

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TO ALL WHOM IT MAY CONCERN:

Be it known that WE, Emmanuel Custodero, Laure Simonot and Jean-Claude Tardivat, citizens of France, whose post office addresses are 5, rue Diderot, F-63400 Chamalieres, France; 68, rue de Wailly, F-63000 Clermont-Ferrand, France; and 7, rue du Dr. Chibret, F-63000 Clermont-Ferrand, France respectively, have invented an improvement in

RUBBER COMPOSITION FOR TIRES, REINFORCED WITH A CARBON BLACK COATED WITH AN ALUMINOUS LAYER

of which the following is a

SPECIFICATION

BACKGROUND OF INVENTION

The present application is a continuation of PCT/EP98/07679, filed November 27, 1998, now WO 99/28380.

The present invention relates to diene rubber compositions which can be used for the manufacture of tires or semi-finished products for tires, in particular treads for these tires, and to reinforcing fillers capable of reinforcing such rubber compositions.

In order to reduce fuel consumption and the pollution emitted by motor vehicles, major attempts have been made by tire designers to obtain tires having all of the following

characteristics: very low rolling resistance, improved grip both on dry ground and on wet or snow-covered ground, and very good wear resistance.

Numerous solutions have thus been proposed to lower the rolling resistance and to improve the grip of tires, but these have generally resulted in a very great decline in the wear resistance.

It is well known that the incorporation of conventional white fillers, such as silica (SiO_2), alumina (Al_2O_3), titanium oxide (TiO_2), chalk, talc, clays such as bentonite or kaolin for example, in rubber compositions used for the manufacture of tires and, in particular, of treads, results in a reduction in the rolling resistance and an improvement in grip to wet, snow-covered or icy ground. However, it also results in an unacceptable decline in the wear resistance because these conventional white fillers do not have sufficient reinforcement ability with respect to such rubber compositions. For this reason, these white fillers are generally referred to as non-reinforcing fillers, or alternatively inert fillers.

One effective solution to this problem was described in Patent Application EP-A-0 501 227, which discloses a special diene rubber composition, reinforced with a highly dispersible precipitated silica. This composition makes it possible to manufacture a tire having substantially improved rolling resistance, without affecting the other properties, in particular those of grip, endurance and, above all, wear resistance.

Since the publication of EP-A-0 501 227, interest in silica-reinforced compositions has been very largely revived. However, silicas are generally more difficult to

disperse than carbon blacks. Furthermore, compositions filled with silica, compared with those filled with carbon black, are known to have the disadvantage of (1) being more difficult to work (i.e. suitability for transformation or "processability") in the uncured state and (2) having a very high electrical resistance.

Compositions that have both improved hysteresis and gripping properties, but which are also easy to work in the uncured state, have a high level of reinforcement and hence of wear resistance, and also high electrical conductivity are therefore extremely desirable to tire manufacturers.

During the course of their research, the Inventors have discovered a novel composition which, due to a specific reinforcing filler, unexpectedly makes it possible to satisfy these different contradictory requirements.

SUMMARY OF THE INVENTION

The invention relates to a sulphur-vulcanizable rubber composition which can be used for the manufacture of tires, comprising at least one diene elastomer, a reinforcing filler and a coupling agent linking the reinforcing filler and the elastomer. This composition is characterized in that the reinforcing filler is formed in its entirety or in part by a "modified" carbon black having the following characteristics:

(i) it is coated at least in part with a layer of aluminium oxide and/or hydroxide;

(ii) its specific BET surface area is between 30 and 400 m^2/g;

(iii) its average particle size (by weight), d_W, is between 20 and 400 nm;

(iv) its disagglomeration rate, α, measured via an ultrasound disagglomeration test, at 10% power of a 600-watt ultrasonic probe, is greater than $1x10^{-3}$ $\mu m^{-1}/s$.

As a result of this modified black and its specific combination of characteristics, notably its particular surface properties, the compositions of the invention have not only improved hysteresis and grip properties, but also high electrical conductivity.

Although rubber compositions comprising carbon blacks having a modified surface and coated by a siliceous layer as reinforcing filler have been described in recent patent publications (see, for example, EP-A-0 711 805, EP-A-0 799 854, EP-A-0 799 867, WO96/037547). However, these novel compositions and their potential for use in tires are still little-known to tire manufacturers. Compared with the compositions filled with carbon blacks coated by a siliceous layer, the compositions of the invention have the significant advantage that the aluminous surface layer deposited on the surface of their reinforcing filler, formed of aluminium oxides and/or hydroxides which, in known manner, are more stable and chemically more reactive than silicon oxides, will consequently adhere better to the particles of black and

will be more reactive than a siliceous layer can be. Furthermore, compared with silica-filled compositions, even those filled with highly dispersible silica, the compositions of the invention have the advantage of having easier working in the uncured state.

Patent Application WO97/42256 describes diene rubber compositions which may incorporate as reinforcing filler carbon blacks treated directly in the carbon black synthesis reactor with various metal compounds in the form, of oxides, hydroxides or carbides of different metals (for example aluminium, zinc, magnesium, calcium, titanium, vanadium, cobalt, nickel, zirconium, tin, antimony, chromium, neodymium, lead, tellurium, barium, caesium, iron and molybdenum). The blacks thus treated at very high temperature in the synthesis reactor consist of hybrid aggregates or particles having two phases, formed by a thorough mixture of carbon black and metal compound, with the metal compound being located both in the interior and close to the surface of the aggregates. It is specified that the content of metal atom may form 50% or even 99% of the mass of the final aggregate (% by mass). It will be understood that such hybrid fillers, if they were in some way freed of their metal compound fraction, for example by suitable chemical treatment, would have neither the morphology nor the properties of a conventional carbon black, but those of high-porosity carbon-containing residues. The treated carbon blacks described in WO97/42256 must not be confused with carbon blacks coated solely with a layer of metal compound which, once such a coating had been eliminated, resume their initial structures.

Furthermore, nothing is said in WO97/42256 about a rubber composition according to the invention, filled with a modified carbon black having the afore-mentioned

specific characteristics of BET surface area, particle size d_W and disagglomeration rate α.

Another subject of the invention is the use of a rubber composition according to the invention in the manufacture of rubber articles, in particular tires or semi-finished rubber products intended for such tires. These semi-finished articles are selected from among the group consisting of treads, underlayers intended for example to be positioned beneath these treads, crown plies, sidewalls, carcass plies, beads, protectors, inner tubes and airtight internal rubbers for tubeless tires. The invention relates more particularly to the use of such a rubber composition for the manufacture of the sidewalls or treads, owing to its good hysteretic properties.

The subject of the invention is also such tires and rubber articles themselves when they comprise a rubber composition according to the invention.

The composition according to the invention is particularly suitable for the manufacture of treads for tires intended to be fitted on passenger vehicles, vans, two-wheelers and heavy vehicles, aircraft, or construction, agricultural or handling machinery, wherein such treads are usable in the manufacture of new tires or for recapping worn tires.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention and its advantages will be readily understood in light of the description and examples which follow, and the drawings in which:

- Figure 1 is a diagram of a device suitable for measuring the ultrasound disagglomeration rate (α) of a filler in the form of agglomerates; and

- Figures 2 and 3 depict curves of the change in the size of the agglomerates during ultrasound generation using the device of Figure 1, for fillers whether or not in accordance with the invention, from which curves the disagglomeration rate (α) is determined.

DETAILED DESCRIPTION

I. MEASUREMENTS AND TESTS USED

I-1. Characterization of the reinforcing fillers

The reinforcing fillers used are characterized as indicated hereafter.

a) BET Specific Surface Area:

The BET specific surface area is determined in known manner, in accordance with the method of Brunauer, Emmet and Teller described in *"The Journal of the American Chemical Society"*, vol. 60, page 309, February 1938, corresponding to Standard AFNOR-NF-T45-007 (November 1987).

b) Average Size of the Particles d_w:

The average size (by mass) of the particles, d_w, is measured after dispersion of the filler, by ultrasound disagglomeration, with the analysis being carried out in an aqueous solution containing 15% ethanol and 0.05% of a non-ionic surfactant (% by volume).

The term "particle" as used in the present application is understood to mean "aggregate", and not that of a possible elementary particle which may form part of this aggregate ("aggregate" is understood, in known manner, to mean a non-splittable unit of elementary

particles, produced during synthesis of the filler).

The determination uses a centrifugal photosedimentometer type "DCP" ("Disk Centrifuge Photosedimentometer", sold by Brookhaven Instruments). A suspension of 10 mg of carbon black is first produced in 40 ml of an aqueous solution containing 15% ethanol and 0.05% of a non-ionic surfactant (% by volume), by action over 10 minutes at 60% power (or 60 % of the maximum position of the "tip amplitude") of a 600-watt ultrasonic probe (a Vibracell one-half inch ultrasound generator sold by Bioblock). During ultrasound generation, a gradient composed of 15 ml water (with 0.05% of a non-ionic surfactant) and 1 ml ethanol is injected into the disc of the sedimentometer rotating at 8000 rpm in order to form a *"step gradient"*. Then, 0.3 ml of the suspension of carbon black is injected at the surface of the gradient. After sedimentation for 120 minutes, the mass distribution of the particle sizes and the average size by mass d_W ($d_W = S(n_i d_i^5) / S(n_i d_i^4)$ with n_i being the number of objects of the size class d_i) are calculated by the software of the sedimentometer.

c) Disagglomeration Rate α:

The disagglomeration rate, α, is measured in what is called the "ultrasound disagglomeration test", at 10% power of a 600-watt probe. This test makes it possible to continuously measure the evolution of the size of the agglomerates of particles during ultrasound generation, as indicated below.

The setup used is formed by a laser granulometer ("Mastersizer S", sold by Malvern Instruments - He-Ne red laser source, wavelength 632.8 nm) and its preparer ("Malvern

Small Sample Unit MSX1"), between which there has been inserted a continuous-flow treatment cell (Bioblock M72410) provided with an ultrasonic probe (600-watt ½ inch ultrasound generator type Vibracell sold by Bioblock).

A small quantity (15 mg) of filler to be analysed is introduced into the preparer with 160 ml of an aqueous solution containing 20% by mass ethanol, with the rate of circulation being set to its maximum. At least three consecutive measurements are taken to determine the initial mean diameter (by volume) of the agglomerates, referred to as $d_V[0]$, in accordance with the known Fraunhofer calculation method (Malvern 3$$D calculation matrix). The ultrasound generation is then set at a power of 10% (or 10% of the maximum position of the "tip amplitude") and the evolution of the mean diameter in volume $d_V[t]$ as a function of the time "t" is monitored for about 8 minutes with one measurement approximately every 10 seconds. After an induction period of about 3 minutes, it was noted that the reciprocal of the mean diameter in volume $1/d_V[t]$ varies linearly with the time "t" (steady state conditions of disagglomeration). The disagglomeration rate α is calculated by linear regression of the curve of evolution of $1/d_V[t]$ as a function of the time "t", within the zone of steady state conditions of disagglomeration. It is expressed in $\mu m^{-1}/s$.

By way of example and as reference, the ultrasound disagglomeration test above, applied to a control silica well-known to the person skilled in the art for its very good dispersibility (silica sold by Rhône-Poulenc under the reference Zeosil 1165MP), results in a disagglomeration rate, α, of approximately $1.5 \times 10^{-3}\ \mu m^{-1}/s$.

Figure 1 shows an example of the setup of the measuring device which can be used for performing this ultrasound disagglomeration test. This device consists of a closed circuit 1 within which a flow 2 of agglomerates of particles suspended in a liquid 3 can circulate. This device comprises a sample preparer 10, a laser granulometer 20 and a treatment cell 30. A vent to atmospheric pressure (13, 33), at the level of the sample preparer 10 and of the treatment cell 30 itself, permits continuous elimination of the air bubbles which form during ultrasound generation (i.e. the action of the ultrasonic probe).

The sample preparer 10 ("Malvern Small Sample Unit MSX1") is intended to receive the sample of filler to be tested (as it is, or already in suspension in the liquid 3) and to send it through the circuit 1 at a controlled speed (potentiometer 17), in the form of a flow 2 of liquid suspension. This preparer 10 is simply a receiving tank which contains, and through which circulates, the suspension to be analysed. It is equipped with a stirrer motor 15, of variable speed, in order to prevent sedimentation of the agglomerates of particles of the suspension. A centrifugal mini-pump 16 is intended to circulate the suspension 2 in the circuit 1. The entrance 11 to the preparer 10 is connected to the open air by an opening 13 intended to receive the sample of filler to be tested and/or the liquid 3 used for the suspension.

A laser granulometer 20 ("Mastersizer S"), is connected to the preparer 10, the role of which is to measure continuously, at regular time intervals, the average size "d_V" of the agglomerates as the flow 2 passes, by means of a measuring cell 23 to which are coupled the automatic recording and calculation means of the granulometer 20. It should be recalled here

briefly that laser granulometers utilize, in known manner, the principle of diffraction of light by solid objects suspended in a medium, the refractive index of which differs from that of the solid. According to the theory of Fraunhofer, there is a relationship between the size of the object and the angle of diffraction of light (the smaller the object, the greater the angle of diffraction). In practice, it is sufficient to measure the amount of light diffracted for different angles of diffraction to be able to determine the size distribution (by volume) of the sample, d_V corresponding to the mean of this distribution ($d_V = S(n_i\, d_i^4) / S(n_i\, d_i^3)$with n_i = number of objects of the size class d_i).

Finally, treatment cell 30 equipped with an ultrasonic probe 35 (converter 34 and probe head 36) intended continuously to break up the agglomerates of particles as the flow 2 passes is inserted between the preparer 10 and the laser granulometer 20.

It is preferred that the treatment cell 30 be arranged between the outlet 22 of the granulometer 20 and the inlet 11 to the preparer 10, such that, during operation, the flow 2 of particles emerging from the preparer 10 first passes through the laser granulometer 20, before entering the treatment cell 30. This arrangement has two major advantages for measurements: first, the air bubbles due to the action of the ultrasonic probe are eliminated on passing through the preparer 10 (which is in the open air), i.e., before entering the granulometer 20; and, therefore, do not upset the laser diffraction measurement; and second, the homogeneity of the suspension is improved by first passing through the preparer 10.

The treatment cell 30 is preferably arranged such that the flow 2 of particles

which penetrates therein via an inlet 31, first passes in front of the head 36 of the ultrasonic probe 35. This non-conventional arrangement wherein the flow 2 enters through the bottom 31 of the cell, and not through the top 32 has the following advantages: first, the entire circulating suspension 2 is forced to pass in front of the end 36 of the ultrasonic probe 35, which is the most active zone in terms of disagglomeration; and second, this arrangement permits initial degasification after ultrasound generation within the body of the treatment cell 30 itself, the surface of the suspension 2 then being in contact with the atmosphere by means of a tube 33 of small diameter.

The flow 2 is preferably thermostatically controlled by means of a cooling circuit 40 arranged, at the level of the cell 30, in a double casing surrounding the probe 35, with the temperature being controlled, for example, by a heat sensor 14 immersed in the liquid 3 at the level of the preparer 10. The arrangement of the various elements of the measuring device is optimized so as to restrict as far as possible the circulating volume, that is to say, the length of the connecting tubes (for example, flexible tubes).

I-2. Characterization of the rubber compositions

The rubber compositions are characterized, before and after curing, as indicated below.

a) Mooney Plasticity:

An oscillating consistometer such as described in standard AFNOR-NF-T43-005

(November 1980) is used. The Mooney plasticity is measured in accordance with the following principle: the uncured mix is molded in a cylindrical enclosure heated to 100°C. After preheating for one minute, the rotor turns within the test piece at 2 rpm, and the torque used for maintaining this movement is measured after four minutes' rotation. The Mooney plasticity (MS 1+4) is expressed in "Mooney units" (MU).

b) Tensile Tests:

These tests make it possible to determine the elasticity stresses and the breaking properties. Unless indicated otherwise, they are carried out in accordance with the standard AFNOR-NF-T46-002 of September 1988.

The secant moduli at 10% elongation (M10), 100% elongation (M100) and 300% elongation (M300) are measured in a second elongation (i.e. after an accommodation cycle), calculated reduced to the real section of the test piece. All these tensile measurements are carried out under normal conditions of temperature and humidity in accordance with the standard AFNOR-NF-T40-101 (December 1979).

c) Hysteresis Losses:

The hysteresis losses (HL) are measured by rebound at 60°C at the sixth impact, and are expressed in % in accordance with the following equation:

$HL (\%) = 100 [(W_0 - W_1) / W_0]$, where W_0 : energy supplied; W_1 : energy restored.

d) Dynamic Properties:

The dynamic properties, referred to as ΔG^* and $\tan(\delta)_{max}$,

measured as a function of the deformation, are carried out at 10 Hertz with a peak-to-peak deformation of 0.15% to 50%. The non-linearity ΔG^* is the difference in the shear modulus between 0.15% and 50% deformation, expressed in MPa. The hysteresis is expressed by the measurement of $\tan(\delta)_{max}$ which corresponds to the maximum of $\tan(\delta)$.

II. CONDITIONS OF CARRYING OUT THE INVENTION

In addition to the usual additives or those capable of being used in a sulphur-vulcanizable rubber composition which can be used for the manufacture of tires, the compositions according to the invention comprise, as base constituents, at least one diene elastomer, a reinforcing filler and a coupling agent between the reinforcing filler and the elastomer, said reinforcing filler being formed in its entirety or in part by a modified carbon black in accordance with the invention.

II-1. Diene elastomer

"Diene" elastomer or rubber is understood to mean, in known manner, an elastomer resulting at least in part (i.e. a homopolymer or a copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not).

Generally, "essentially unsaturated" diene elastomer is understood to mean a diene elastomer resulting at least in part from conjugated diene monomers having a content of members or units of diene origin (conjugated dienes) which is greater than 15% (mole %).

Thus, for example, diene elastomers such as butyl rubbers or copolymers of dienes and of alpha-olefins of the EPDM type do not fall within the preceding definition, and may in particular be described as "essentially saturated" diene elastomers (low or very low content of units of diene origin which is always less than 15%).

Within the category of "essentially unsaturated" diene elastomers, "highly unsaturated" diene elastomer is understood to mean a diene elastomer having a content of units of diene origin (conjugated dienes) which is greater than 50%.

These definitions being given, the following are understood in particular to be meant by diene elastomer capable of being used in the compositions according to the invention:

(a) any homopolymer obtained by polymerization of a conjugated diene monomer having 4 to 12 carbon atoms;

(b) any copolymer obtained by copolymerization of one or more dienes conjugated together or with one or more vinyl aromatic compounds having 8 to 20 carbon atoms;

(c) any ternary copolymer obtained by copolymerization of ethylene, and an α-olefin having 3 to 6 carbon atoms with a non-conjugated diene monomer having 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene, from propylene with a non-

conjugated diene monomer of the aforementioned type, including *inter alia* 1,4-hexadiene, ethylidene norbornene or icyclopentadiene;

(d) any copolymer of isobutene and isoprene (butyl rubber), as well as halogenated, in particular chlorinated or brominated, versions of this type of copolymer.

Although it applies to any type of diene elastomer, the person skilled in the art of tires will understand that the present invention is used primarily with essentially unsaturated diene elastomers, in particular those of type (a) or (b) above.

Suitable conjugated dienes are, in particular, 1,3-butadiene, 2-methyl-1,3-butadiene, the 2,3-di(C_1 to C_5 alkyl)-1,3-butadienes such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene.

Suitable vinyl aromatic compounds are, in particular, styrene, ortho-, meta- and para-methylstyrene, the commercial mixture "vinyl-toluene", para-tertiobutylstyrene, the methoxy-styrenes, the chloro-styrenes, vinyl mesitylene, divinyl benzene and vinyl naphthalene.

The copolymers comprise between 99% and 20% by weight of diene units and between 1% and 80% by weight of vinyl aromatic units. The elastomers may have any

microstructure, which is a function of the polymerization conditions used, in particular of the presence or absence of a modifying and/or randomizing agent and the quantities of modifying and/or randomizing agent used. The elastomers may, for example, be block, statistical, sequenced or microsequenced elastomers, and may be prepared in dispersion or in solution.

Polybutadienes are preferred, particularly those having a 1,2 bond content of between 4% and 80% and those having a content of cis-1,4 bonds of more than 90%, polyisoprenes; butadiene-styrene copolymers, and in particular those having a styrene content of between 5% and 50% by weight and, more particularly, between 20% and 40% by weight, a 1,2 bond content of the butadiene part of between 4% and 65%, and a content of trans-1,4 bonds of between 20% and 80%; butadiene-isoprene copolymers, particularly those having an isoprene content of between 5% and 90% by weight and a glass transition temperature (Tg) of -40°C to -80°C and isoprene-styrene copolymers, particularly those having a styrene content of between 5% and 50% by weight and a Tg of between -25°C and -50°C.

In the case of butadiene-styrene-isoprene copolymers, there are suitable in particular those having a styrene content of between 5% and 50% by weight and, more particularly, between 10% and 40%, an isoprene content of between 15% and 60% by weight, and more particularly between 20% and 50%, a butadiene content of between 5% and 50% by weight, and more particularly between 20% and 40%, a content of 1,2-units of the butadiene part

of between 4% and 85%, a content of trans-1,4 units of the butadiene part of between 6% and 80%, a content of 1,2- plus 3,4-units of the isoprene part of between 5% and 70%, and a content of trans-1,4 units of the isoprene part of between 10% and 50%, and more generally any butadiene-styrene-isoprene copolymer having a Tg of between -20°C and -70°C, and more generally any butadiene-styrene-isoprene copolymer having a Tg of between 20°C and -70°C.

The elastomer may be coupled and/or starred or alternatively functionalized with a coupling and/or starring or functionalizing agent. The elastomer may also be natural rubber or a blend based on natural rubber with any synthetic elastomer, in particular a diene elasomer.

In particular, the diene elastomer of the composition of the invention is selected from among highly unsaturated diene elastomers which include polybutadienes, polyisoprenes or natural rubber, butadiene-styrene copolymers, butadiene-isoprene copolymers, isoprene-styrene copolymers, butadiene-styrene-isoprene copolymers, or a mixture of two or more of these elastomers.

When the composition of the invention is intended for a tread for a tire, the diene elastomer is preferably a butadiene-styrene copolymer prepared in solution having a styrene content of between 20% and 30% by weight, a content of vinyl bonds of the butadiene part of between 15% and 65%, a content of trans-1,4 bonds of between 20% and 75%, and a glass

transition temperature Tg of between -20°C and -55°C. This butadiene-styrene copolymer may also be used in a mixture with a polybutadiene having preferably more than 90% cis-1,4 bonds.

II-2. Reinforcing filler

The composition according to the invention is reinforced, at least in part, by a carbon black having a modified surface, referred to as "modified carbon black" or "modified black", having the following characteristics:

(i) it is coated at least in part with a layer of aluminium oxide and/or hydroxide;

(ii) its specific BET surface area is between 30 and 400 m^2/g;

(iii) its average particle size (by mass), referred to as d_w, is between 20 and 400 nm;

(iv) its disagglomeration rate, α, measured via the ultrasound disagglomeration test, at 10% power of a 600-watt ultrasonic probe, is greater than 1×10^{-3} $\mu m^{-1}/s$.

"Aluminium oxide and/or hydroxide" is understood to mean any aluminium compound corresponding, with the exception of any impurities and the water of hydration, to the general Formula (I) below (a and b being real numbers):

$$\text{(I)} \quad Al(OH)_a O_b, \quad \text{where:} \quad 0 < a \leq 3 \quad \text{and } b = (3-a)/2.$$

Such a formula covers pure aluminium oxides or aluminas, Al_2O_3 (a=0); aluminium trihydroxides, $Al(OH)_3$ (a=3); intermediate oxide/hydroxides ($0<a<3$) and the hydrated forms thereof; or a mixture of aluminium trihydroxides and/or oxide-hydroxides. This formula is given with the exception of any impurities, it being understood that the aluminium oxides and/or hydroxides present on the surface of the modified carbon black may comprise a certain proportion of impurities resulting from the processes used for manufacturing the filler.

It is generally known that in order to obtain the optimum reinforcement properties imparted by a filler, it is advantageous for the filler to be present in the rubber matrix in a final form which is both as finely divided as possible and is distributed as homogenously as possible. Currently, such conditions may be obtained only if the filler (1) has a very good ability to be incorporated into the matrix during mixing with the elastomer and (2) to disagglomerates in order to disperse homogenously in the elastomer.

The intrinsic dispersibility of a filler can be evaluated via the ultrasound disagglomeration test described in Section I above, by measuring its disagglomeration rate α.

It has been found that, for a rate a greater than 1×10^{-3} $\mu m^{-1}/s$, the modified black has good dispersibility, i.e., that few micronic agglomerates are observed by reflection in optical microscopy on a section of rubber composition prepared according to known techniques.

For even better dispersion of the modified black in the diene rubber matrix, which provides for optimum reinforcement, it is preferred that the disagglomeration rate α be greater than

$1.5x10^{-3}$ $\mu m^{-1}/s$. This is particularly advantageous when the invention is used for manufacturing treads having a low rolling resistance.

Where the BET surface area is less than 30 m²/g, the rubber compositions have easier working (suitability for transformation or "processability") and a reduced hysteresis, but exhibit a decline in the breaking and wear resistance properties in the tire comprising such fillers; where the BET surface areas are greater than 400 m²/g, working in the uncured state becomes more difficult (higher Mooney plasticity) and the dispersion of the filler is adversely affected as a result. For excessively large sizes where d_w, is greater than 400 nm, the particles act like defects which localize stresses and are harmful in terms of wear, where sizes d_w are too small, i.e., less than 20 nm, on the other hand, working in the uncured state and the dispersion of the filler during this working are impaired.

For all the reasons set forth above, the BET surface area preferably ranges from 50 to 300 m²/g and the particle size d_w preferably ranges from 30 to 200 nm.

Because of its aluminous surface layer, the modified carbon black has high surface reactivity, i.e. a high amount of surface functions (Al-OH) which are reactive to the coupling agent (filler/elastomer). This is particularly beneficial to the mechanical properties of the rubber compositions of the invention, i.e., to the reinforcement function performed by the filler.

Preferably, the amount of aluminium (of the element Al) present on the surface of the modified carbon black is greater than 0.25%, more preferably greater than 0.5%, and even

more preferably ranges between 0.5% and 5% (% by weight of modified black, determined by chemical analysis).

Below the minima indicated, the effect of lowering the hysteresis may be inadequate, depending on the nature of the compositions used, particularly the elastomer. Beyond the maximum amount advocated generally no further improvement in the hysteresis is observed, whereas there is a risk of (1) poor dispersibility of the modified black, a known disadvantage of white fillers relative to the carbon black, and (2) a reduction of the adhesion of the aluminous layer to the surface of the carbon black. An amount of more than 5% aluminum also requires larger quantities of precursor product (aluminium alkoxide), and, even, longer impregnation times during manufacture, which is economically less advantageous.

To optimize the adhesion of the aluminous layer to the surface of the black and the dispersibility of the filler in the rubber composition, particularly when the composition is intended for a tread for a tire having low rolling resistance, it is preferred that the amount of aluminium be between 0.5% and 3%.

The modified black may be used alone or associated with another reinforcing filler, for example a reinforcing silica. Preferably, a highly dispersible precipitated silica is used, in particular when the invention is used to manufacture tires having a low rolling resistance. Non-limiting examples of such preferred highly dispersible silicas, include the silica Perkasil KS 430 from Akzo, the silica BV 3380 from Degussa, the silicas Zeosil 1165 MP and 1115 MP from Rhône-Poulenc, the silica Hi-Sil 2000 from PPG, and the silicas Zeopol 8741 or 8745 from

Huber.

The modified black, alone or associated with silica, may also be used in a blend, i.e., in a mixture, with conventional carbon black.

Preferably, in the compositions according to the invention, the modified black constitutes the majority, i.e. more than 50% by weight, of the total reinforcing filler. Advantageously, the modified black constitutes the entire reinforcing filler.

Preferably, the amount of total reinforcing white filler in the compositions of the invention is in a range from 20 to 300 phr (parts by weight per 100 parts elastomer), more preferably from 30 to 150 phr, the optimum differing according to the intended applications. For example, the level of reinforcement expected for a bicycle tire, for example, is distinctly lower than that required for a tire for a passenger vehicle or for a utility vehicle such as a heavy vehicle.

Synthesis of the modified black

The modified carbon black may be prepared by the following process:

a) impregnating a tire-grade carbon black with a collodal suspension formed by hydrolysis of a solution of aluminum alkoxide in an alcoholic solvent;

b) removing the alcoholic solvent by evaporation; and

c) treating the impregnated black so as to transform the aluminous layer present at its surface into an adhering layer of aluminium oxide and/or hydroxide.

Suitable carbon blacks include all the reinforcing carbon blacks conventionally used in tires, in particular in treads for these tires. Particular blacks include HAF ("High

Abrasion Furnace"), ISAF ("Intermediate Super Abrasion Furnace") and SAF ("Super Abrasion Furnace"). Of the latter, reference will more particularly be made to the reinforcing carbon blacks of series 100, 200 or 300 (ASTM grades).

Preferably, the carbon blacks have the following characteristics:

- a BET surface area of between 20 and 200 m^2/g, and more preferably between 50 and 170 m^2/g ;

- an average particle size (by mass), d_W, of between 20 and 400 nm, and more preferably between 30 and 200 nm.

Non-limiting examples of preferred starting blacks, include the blacks N115, N134, N234, N339, N347 and N375.

"Colloidal suspension" is understood to mean a suspension of solid phase in a liquid, where the size of the solids is less than a micrometer (μm). To form the impregnating colloidal suspension, an aluminium alkoxide is dissolved, with stirring and heating, in a selected alcohol, for example methanol, ethanol, (iso)propanol or the various isomers of butanol. Next, the entire solution is hydrolyzed by adding water. The aluminium alkoxide used is preferably an aluminium alkoxide comprising 1 to 6 carbon atoms, for example a methoxide, an ethoxide, an (iso)propoxide, the butoxides of aluminium, or a mixture of two or more of these compounds.

The impregnation stage may be performed at ambient temperature (20°C) or at a higher temperature, for example between 30°C and 65°C, depending on the nature of the alcohol or alcohols used. The temperature should be lower than the boiling temperature of the

suspension. However, the selected temperature may be close to this boiling temperature. The impregnation time, from several minutes to several hours, is selected to be sufficiently long, enough to create sufficient physical-chemical interactions between the surface of the carbon black and the aluminium-based compound.

Preferably, the impregnating colloidal suspension comprises nitric acid which is used both as a hydrolysis catalyst for the alkoxide solution and as peptizing agent for the colloidal suspension. After reaction, the nitric acid is removed by washing the impregnated black with water. The elimination of the alcoholic solvent, after impregnation of the carbon black, is carried out by any appropriate means, for example by vacuum evacuation, with stirring.

The treatment stage is preferably a heat treatment carried out under inert gas, for example argon, at a temperature preferably between 100°C and 900°C, and more preferably between 150°C and 850°C. Generally, the higher the temperature, the more the compound of Formula (I)"shifts" from hydroxide towards oxide (reduction of a and increase in b). For example, treatment at a temperature of 800-850°C, results in an aluminous layer that is essentially alumina (Al_2O_3).

II-3. Coupling agent

When a reinforcing silica is used, it is well-known to the person skilled in the art to use a (silica/elastomer) coupling agent, also referred to as a bonding agent, the role of which is to produce a bond between the white filler and the elastomer, while facilitating the dispersion of this white filler within the elastomeric matrix must also be used.

The modified black, because of its aluminous surface layer, also requires the use of such a coupling agent in order fully to perform its function of reinforcing filler in the rubber composition according to the invention.

"Coupling" agent (filler/elastomer) is more precisely understood to mean an agent capable of establishing a sufficient chemical and/or physical connection between the white filler and the elastomer, while facilitating the dispersion of the white filler within the elastomeric matrix. Such a coupling agent, which is at least bifunctional, has, for example, the general formula "Y-T-X", in which:

- Y represents a functional group ("Y" function) which is capable of bonding physically and/or chemically with the white filler, such a bond being able to be established, for example, between a silicon atom of the coupling agent and the hydroxyl (OH) surface groups of the white filler (for example, surface silanols in the case of silica);

- X represents a functional group ("X" function) which is capable of bonding physically and/or chemically with the elastomer, for example by means of a sulphur atom; and

- T represents a hydrocarbon group that links Y and X.

The coupling agents are not to be confused with simple agents for covering the white filler which, in known manner, comprise the Y function which is active with respect to the white filler, but are devoid of the X function which is active with respect to the elastomer.

The modified black, because of its aluminous surface layer, also requires the use of such a coupling agent in order fully to perform its function of reinforcing filler in the rubber composition according to the invention.

Coupling agents, of variable effectiveness, have been described in a number of documents, for example Patents US-A-3 842 111, US-A-3 873 489, US-A-3 978 103, US-A-3 997 581, US-A-4 002 594 as well as US-A-5 580 919, US-A-5 583 245, US-A-5 663 396, US-A-5 684 171, US-A-5 684 172, US-A-5 696 197, which describe such known compounds in detail.

In fact, any known coupling agent may be used to ensure, in diene rubber compositions which can be used for the manufacture of tires, effective bonding or coupling between the silica and diene elastomer. Such coupling agents include organosilanes, in particular polysulphurized alkoxysilane such as polysulphides, in particular tetrasulphides, bis(trialkoxy(C_1-C_4)-silylpropyl), in particular bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl). In particular, bis(3-triethoxysilylpropyl) tetrasulphide, abbreviated TESPT, of the formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, sold, for example by Degussa under the name Si69, is used.

The person skilled in the art will be able to adjust the content of coupling agent in

the compositions of the invention, according to the intended application, the nature of the polymer used, and the quantity of modified black used, optionally supplemented by any reinforcing white filler used as complementary filler.

So as to allow for the differences in specific surface area and density of the reinforcing fillers which may be used, as well as the molar masses of the coupling agents, it is preferable to determine the optimum amount of coupling agent, for the modified black, in moles per square meter of modified black. This optimum amount is calculated from the weight ratio [coupling agent/modified black], the BET surface area of the modified black and the molar mass of the coupling agent (referred to as *M* hereafter), according to the following equation:

$$(\text{moles/m}^2 \text{ modified black}) = [\text{coupling agent / modified black}]\ (1/\text{BET})\ (1/M)$$

An equivalent relationship is applied, for example, to silica if it is used as complementary reinforcing white filler, in order also to determine the maximum amount of additional coupling agent for this silica, in moles per metre squared of this white filler.

Preferably, the (total) quantity of coupling agent used in the compositions according to the invention is between 10^{-7} and 10^{-5} moles per square meter of [modified carbon black, plus optional associated reinforcing white filler]. More preferably the amount of coupling agent is between $5\text{x}10^{-7}$ and $5\text{x}10^{-6}$ moles per square meter of [modified carbon black, plus optional associated reinforcing white filler].

II-4. Various additives

The compositions according to the invention contain, in addition to the compounds already described, all or part of the constituents usually used in diene rubber compositions intended for the manufacture of tires, such as plasticizers, pigments, antioxidants, antiozonants, a cross-linking system based either on sulphur or on sulphur and/or peroxide and/or bismaleimide donors, vulcanziation accelerators, extending oils, etc.

The compositions according to the invention might also contain, in addition to the coupling agents described above, covering agents for white filler, such as alkylalkoxysilanes, polyols or amines.

The compositions according to the invention may be used alone or in a blend with any other rubber composition which can be used for manufacturing tires.

II-5. Preparation of the compositions

The rubber compositions are prepared using the diene polymers according to known techniques, for example by thermomechanical working in one or two stages in a internal paddle mixer, followed by mixing on an external mixer.

According to a conventional one-stage process, all the constituents necessary, with the exception of the vulcanziation system, are introduced into a conventional internal mixer. The result of this first mixing stage is then taken up on an external mixer, generally an open mill, and then the vulcanziation system is added thereto. A second stage may be added in the internal mixer, essentially with the aim of making the mixture undergo complementary heat treatment.

III. EXAMPLES

III-1. Synthesis of the modified black

The synthesis of the modified black was carried out according to paragraph II-2 of Section II above, using the specific conditions below.

a) Preparation of the Impregnation Solution :

8.0 g of aluminium isopropoxide (98% $Al(OCH(CH_3)_2)_3$, Sigma Chemicals) were dissolved in 200 ml of anhydrous ethanol by magnetic stirring at 500 rpm at a temperature of 60°C. After one hour, 42.4 g of demineralized water was added and stirring was continued at 60°C. Two hours later, 10 ml of concentrated nitric acid (53%) were added and the temperature was gradually lowered to ambient temperature, followed by stirring for 12 hours. Thus, a colloidal suspension was obtained by hydrolysis of the alcoholic solution of aluminium isopropoxide.

b) Impregnation of the Carbon Black:

40 g of carbon black N234 were placed in the flask of a rotary evaporator (Rotavapor R-124 of Büchi, sold by Bioblock). The bath temperature was set at 50°C and the speed of rotation at 80 rpm (time "t" = 0). After stirring for 55 minutes (t = 55 min), a third of the impregnation solution was added, another third was added at t = 85 minutes, and the last third was added at t = 115 minutes. Thus, the stirring was maintained for approximately three hours. A vacuum was then created (t = 5 hours) to remove the excess alcoholic solvent. After 30 minutes, the temperature of the bath was set to 60°C and stirring was thus continued under

vacuum until t = 7 hours, to completely evacuate the solvent. The carbon black thus impregnated is then removed from the flask, placed in a vacuum oven (200 mm Hg) and dried at 100°C for one night. The black thus treated was then extracted by water over 48 hours in a Soxhlet apparatus, then dried again under the same conditions.

c) Heat Treatment:

The impregnated carbon black was then placed in a tubular oven (Carbolite CTF15/75 610, sold by Osi), under a flow of argon (200 ml/min), then subjected to the following thermal cycle: 30 minutes at 200°C, followed by 1 hour at 800°C. The temperature increase ramps were set at 10°C/minute.

The characteristics of the carbon black thus obtained are summarized in Table 1. It should be noted that the particle size d_w is not significantly different from the starting black, but that its BET surface area, is greatly increased i.e., by more than 50%. The amount of aluminium is high, about 1.5%, a result which is well-correlated with the amount of ash measured.

Furthermore, the disagglomeration rate is distinctly greater than the set lower limit of 1×10^{-3} $\mu m^{-1}/s$ (i.e. 2/3 of a_0). A rate α of 3.1×10^{-3} $\mu m^{-1}/s$ must be considered as particularly high, since it is greater by about 100% than the rate α recorded for a highly dispersible control silica (Zeosil 1165MP).

Figures 2 and 3 show the curves of evolution $[1/d_v(t) = f(t)]$ of the size of the agglomerates, recorded in the ultrasound disagglomeration test, respectively for the modified

black and for the highly dispersible control silica (Zeosil 1165MP), where the rate α is determined from the slope of the straight line $[1/d_v(t) = f(t)]$.

It can be seen from Figures 2 and 3 that the first points recorded ("t" varying from 0 to about 30 s) correspond to the measurement of the initial diameter $d_v[0]$, followed (after actuation of the ultrasonic probe) by progressive passage ("t" from 30 s to about 3 min) to steady state conditions of disagglomeration during which the reciprocal of "d_v" varies linearly with the time "t". The recording of the data was stopped after about 8 minutes. The disagglomeration rate α in the zone of steady state conditions of disagglomeration was deduced from this by elementary calculation of linear regression, performed by the calculator of the granulometer.

The starting carbon black N234, in the same ultrasound disagglomeration test, has a particularly high rate a (17×10^{-3} $\mu m^{-1}/s$; not shown in the drawings), which was expected, given the known very high dispersibility of the carbon blacks for tires.

III-2. <u>Preparation of the compositions</u>

The compositions tested hereafter were prepared in known manner in laboratory mixers as follows: The diene elastomer was introduced into an internal mixer filled to 75%, the temperature of which was approximately 70°C. After a suitable kneading time, for example of the order of 1 minute, all the other ingredients, with the exception of the vulcanization system, were added, including the filler and, if applicable, the associated coupling agent. Thermo-mechanical working was then carried out for about 5.5 minutes, at an average paddle speed of 70 rpm until a dropping temperature of about 140°C was reached. The mixture thus obtained was

recovered and the vulcanization system was then added on an external mixer (homo-finisher) at 30°C. Vulcaniziation was carried out at 150°C (40 min).

III-3. Tests

Two diene rubber compositions intended for the manufacture of tires or treads for tires are compared below. The SBR elastomer (styrene-butadiene copolymer) prepared in solution and contains 25% styrene, 58% 1,2-polybutadiene bonds and 23% polybutadiene trans-1,4 bonds.

These 2 compositions are generally identical apart from the following differences in filler:

- composition No. 1 (control): conventional reinforcing filler formed by an N234-type carbon black;
- composition No. 2 (in accordance with the invention): reinforcing filler formed exclusively by the modified carbon black N234, with which there is associated the coupling agent Si69 (TESPT).

The coupling agent Si69 was introduced at a rate corresponding to surface covering of about 9.6×10^{-7} mole/m² of modified carbon black.

Tables 2 and 3 show in succession the formulation of the different compositions (Table 2 - amount of the different products expressed in phr, i.e., parts by weight per 100 parts elastomer), and their properties before and after curing at 150°C for 40 minutes (Table 3).

The following observation may be made:

- The Mooney plasticity value appears lower for the composition according to the invention than for the control composition, which reveals a very good ability of the composition of the invention to be worked in the uncured state.

- The composition according to the invention has moduli values, in particular values of moduli M100 and M300, indicating the quality of reinforcement, which are at least equal to, if not greater, than those obtained on the control composition.

- The composition according to the invention furthermore has very advantageous hysteretic properties, compared with those provided by conventional carbon black, with a very significant reduction in the losses by rebound (HL), in the non-linearity ΔG^* and in $\tan(\delta)_{max}$.

In summary, the compositions of the invention comprising modified carbon black unexpectedly have substantially improved hysteresis properties, without their working properties in the uncured state and reinforcement properties after curing being adversely affected.

These results make it possible to predict both good ability to resist wear and particularly low rolling resistance for tire treads, while guaranteeing these treads satisfactory electrical conductivity which is sufficient to dissipate, for example, electrostatic charges which may form due to friction during rolling of the tires.

It is believed that the specific process for preparing the modified carbon black (impregnation in the cold state followed by heat treatment) makes it possible to deposit on the surface of the particles or aggregates of carbon black a fine aluminous layer which is stable, adheres strongly and is distributed relatively homogenously (average particle size little altered,

but great increase in the BET surface area).

Such a quality of coating of its reinforcing filler might explain the unexpected performance of the rubber composition according to the invention, compared with compositions reinforced with conventional carbon black (drop in hysteresis) and with compositions reinforced with a precipitated silica, even if highly dispersible (increase in dispersibility; high electrical conductivity).

The compositions of the invention thus offer an advantageous alternative to the use of conventional compositions filled with carbon blacks or highly dispersible silicas, or even carbon blacks coated with a siliceous layer.

Table 1

	N234	Modified N234
Ashes 825°C/air (%)	0.06	3.24
Amount of Al (%)	0.03	1.49
He Density (g/ml)	1.9926	2.0329
BET surface area (m^2/g)	117	193
d_w (nm)	65	68
α ($\mu m^{-1}/s$)	0.0174	0.0031

Table 2

Composition number	1	2
SBR (1)	100	100
N234	50	-
Modified N234	-	50
Si69	-	5
ZnO	3	3
Stearic acid	1.5	1.5
Antioxidant (2)	1	1
DPG (3)	0.5	0.5
Sulphur	1.5	1.5
CBS (4)	2	2

(1) butadiene-styrene copolymer

(2) N-1,3-dimethylbutyl N-phenylparaphenylenediamine

(3) Diphenylguanidine

(4) N-cyclohexyl-2-benzothiazylsulphenamide

Table 3

Composition number	1	2
Plasticity (MU)	106	101
M10 (MPa)	6.41	6.27
M100 (MPa)	5.32	5.68
M300 (MPa)	14.09	14.25
HL (%)	31.6	28.1
ΔG^* (MPa)	4.81	3.20
$\tan(\delta)_{max}$	0.345	0.291